

CHAPTER 1

INTRODUCTION

1.1 Background Study

Nanomaterials are increasingly gaining the attention of not only the scientific community but also the public due to their unique properties which endear them to new and exciting applications. These special properties can vary markedly from those of the analogous bulk materials. The physical and chemical properties of the nanomaterials tend to be exceptionally closely dependent on their size and shape or morphology. As a result, materials scientists are focusing their efforts on developing simple and effective methods for synthesizing nanomaterials with controlled size and morphology.

Synthesized and characterized nanomaterials of controlled size and shape have a great potential to be used in several different applications including interconnects in electronic devices with super functions and bio-molecule separations, catalysis etc. There are different synthesis methods for nano sized materials powder. The synthesis methods such as spray pyrolysis, precipitation, sol-gel, hydrothermal and combustion synthesis have been employed to prepare nano sized alumina powder.

By altering the synthesis methods, many researchers were able to create a range of different nanoparticles. These synthesized nanomaterials varied from uniformly sized spherical nanoparticles, nanowires, nanorods to arrays with oriented mesochannels. Once the nanomaterials powders are synthesized, it is then characterized (i.e. determining the particle size, crystal structure etc). Some of the equipments that are mostly used for the characterization of nano particles are X-ray Fluorescence (XRF), Scanning Electro Microscopy (SEM), X-ray Diffractometer (XRD), Fourier transition infra radiation (FTIR), Thermo Gravimetric Analysis (TGA), Brunnauer-Emmet-Teller (BET) and Dynamic Light

scattering(DLS).

Many researches has shown that gel-combustion method is highly suited for the synthesis of nano alumina of high-purity, stable metastable phases and it can also be used to produce any size and shape using relatively simple equipments.

1.2 Problem Statement

Nano alumina powder has lot of applications in different areas, like catalysis, gas separation membrane and electronic materials. Although there are different methods to synthesis nano sized alumina powder like spray pyrolysis, precipitation, sol-gel and hydrothermal, all the methods mentioned are either time or energy consuming. This study is about synthesizing nano-alumina by gel-combustion using Aluminum nitrate and fuels (citric acid and urea) as main starting materials. The gel combustion method is simple, safe way and a rapid synthesis process compared to the others. It can be used to synthesize homogeneous, high-purity, crystalline oxide ceramic powders including nano-alumina powders with a narrow range of particle sizes.

1.3 Objectives

- To prepare nano sized alumina powder by gel-combustion method using aluminium nitrate and two type of fuel (citric acid and urea) as a starting material.
- To characterize the synthesized powder using XRD, SEM, BET and DLS.

1.4 Scope of study

This study involves the synthesis of nano alumina from combustible gels by gel-combustion method which is an exothermic reaction. Aluminum oxide (alumina) is the most widely used oxide ceramic, either in pure form or as raw material to be mixed with other oxides. Alumina (Al_2O_3) has mechanical and physical properties particularly suitable for electrical and thermal insulation, for cutting tools and abrasives. It has very good anti-corrosion properties and also used in catalysis. It can be found in different degrees of purity and crystal structures, with different properties. In its transparent form, alumina can also be used for optical applications.

The combustion synthesis of nano alumina synthesis powders from stoichiometric mixtures of the relevant water-soluble aluminum nitrate as cation precursor and urea and citric acid as fuels will be investigated. This research is an experimental work where preparation of samples is carried out considering some parameters which can affect the size and morphology of the nano particles. These parameters are like the oxidizer to fuel ratio, type of fuel used and PH of the starting solution. In this study, two fuels (i.e urea and citric acid) are compared based on the size of the product. In addition to this, the effect of the PH and oxidizer to fuel ratio on the particle size of alumina particle is studied. Following the synthesis, the samples are characterized using SEM, XRD and DLS to determine particle size, morphology and crystal structure.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Alumina (Al_2O_3) which covers about 20% of the earth's crust occurs both in amorphous-hydrated ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) and crystalline forms (α - Al_2O_3 , β - Al_2O_3 , γ - Al_2O_3 and ζ - Al_2O_3). It is an extremely stable material with versatile properties such as excellent mechanical strength with hardness of 9.0 on Mohs's scale, high melting point (2041°C), and dimensional stability up to 1500°C , chemical inertness to most acids and alkalis and resistance to corrosion in hostile environments. Such unique properties coupled with its low cost makes alumina the most commonly used material for all engineering applications such as electronics, chemical processing, oil and gas processing, refractories, preparation of synthetic gems, wear and corrosion resistance and a wide variety of other industrial processes.

An important development that has hitherto taken place at the industrial floor is the gradual replacement of conventional metal or plastic materials with alumina based ceramic materials. This has tremendously increased the demand for alumina like materials. A lot of activity is therefore directed to the quality production of alumina and its related products like aluminates, garnets, etc. with minimum cost. The manufacture of these products normally requires a high temperature of $>1000^\circ\text{C}$ or special infrastructure which require careful maintenance. In such situation combustion synthesis is a simpler method that can be adopted for the bulk production of high purity alumina and related oxides.

2.2 Synthesis

There are a wide variety of methods available for the preparation of nanomaterials. They include breaking down a bulk solid or building up processes. The characteristics of nano powders are influenced significantly by the synthesis method used. Various chemical methods such as spray pyrolysis, precipitation, sol-gel, hydrothermal and combustion synthesis have been employed to synthesize nano Al_2O_3 powders. All these nano particle synthesis methods require special chemicals and equipments. In the following section, various methods used to produce nano sized particles are discussed briefly.

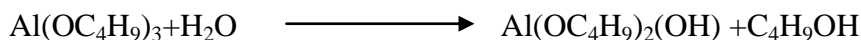
2.2.1 Sol –gel method

The sol-gel process is a wet-chemical technique widely used recently in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers.

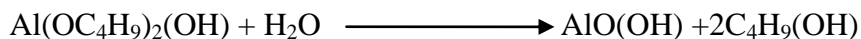
This method is a liquid phase reaction that involves the polymerization of molecules in solutions, which result in the solidification of a sol to a gel. The state in which fine particles (1-100nm in diameter) are dispersed in liquid is called colloid. When the colloid is sufficiently fluid and stable for a long period of time, the colloid is called the sol. Rigid solids formed by the evaporation of a solvent from a sol is called the gel. A gel is a semi rigid colloidal dispersion of solid particles in a liquid. Typically the rigidity of the gel is such that it will not flow under the influence of gravity. Solgel processing that can be done at room temperature involves the formation of dispersion of nanoparticles in gel.

Typical precursors for this method are metal alkoxides and metal chlorides, which undergo various forms of hydrolysis and poly condensation reactions. The formation of a metal oxide involves connecting the metal centers with oxo (M-O-

M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. The metal alkoxide precursors can readily undergo catalyzed hydrolysis and condensation to form a gel of metal oxide nanoparticles. For example, a gel of Al₂O₃ nanoparticles can be made by hydrolysis of aluminum *sec*-butoxide (ASB), Al(OC₄H₉)₃ by the reaction



A catalyst is used to start the reaction and control it. This reaction is followed by the a condensation polymerization



Which is followed by



Thus, the sol evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks.

In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation.

Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final

component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing. Afterwards, a thermal treatment, or firing process, is often necessary in order to favor further poly condensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth.

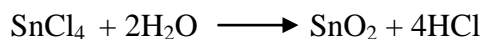
One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.

2.2.2 Spray pyrolysis method

Spray pyrolysis is one type of nano particle synthesizing method where the precursor solution is pulverised as a fine mist via a spray nozzle and a carrier gas at high pressure. The so produced mist condenses on a preheated substrate, and is instantly pyrolysed (spray pyrolysis). The process can be conducted in one or more pulses to obtain uniform films. Spray pyrolysis is suitable for substrates with complex geometry, and can be used for a variety of oxide materials.

The spray pyrolysis equipment comprises a spray nozzle, a rotating heating plate and a container. The whole is mounted in a protective chamber which can be filled with protective or reactive gases. The nozzle is driven pneumatically via a computer controlled control unit.

During the process of synthesizing, thin films are formed on heated substrates by spraying aqueous solutions of metal compounds such as halides. For example, a transparent conductive film of SnO₂ on a glass surface is formed by the following spray pyrolysis reaction:

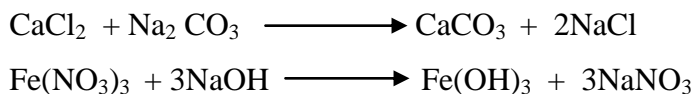


The spray pyrolysis method is simple and also been used for the deposition of ferrite thin films.

2.2.3 Precipitation method

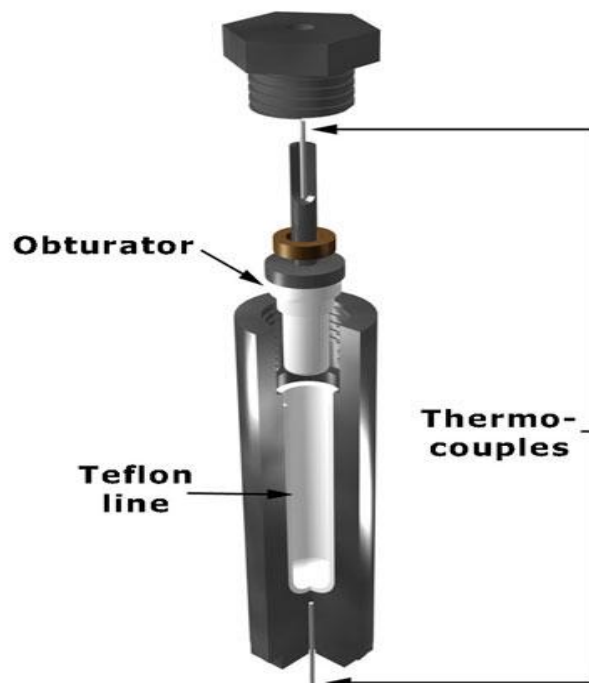
Precipitation is the formation of a solid in a solution during a chemical reaction. When the reaction occurs, the solid formed is called the precipitate, and the liquid remaining above the solid is called the supernate.

When aqueous solutions of various salts react, compounds with low solubility precipitate out of the solution. Ceramic powders can be obtained after washing drying and calcining the precipitates. By employing various salts and controlling processing parameters such as temperature, it is possible to control the particle size of ceramic powders produced. This method is especially suited for the production of fine particles. Examples of the precipitation reactions employed for the production of ceramic powders are:



2.2.4 Hydrothermal method

The term ‘hydrothermal’ came from the earth sciences, where it implied a regime of high temperatures and water pressures. Therefore, it can be defined as a method of synthesis of powders from high-temperature aqueous solutions at high pressures. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave (see figure 1 below), in which a nutrient is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes seeds to take additional growth.



source:<http://www.inorg.chem.msu.ru/matsci/hydrothermal/pict/Autoclave.jpg>

Figure 1. Scheme of the autoclave for hydrothermal synthesis

A large number of compounds belonging to practically all classes have been synthesized under hydrothermal conditions: elements, simple and complex oxides, carbonates, silicates, etc.

Although the hydrothermal method is very versatile, one of the main drawbacks is slow kinetics at any given temperature. In order to increase the kinetics of crystallization, one can introduce microwave or electric or ultrasonic fields in the hydrothermal system and these combinations are termed microwave-hydrothermal, electrochemical-hydrothermal and ultrasonic-hydrothermal methods, respectively.

The other disadvantages of this method are the need of expensive autoclaves, good quality seeds of a fair size and the impossibility of observing the crystal as it grows.

2.2.5 Combustion synthesis method

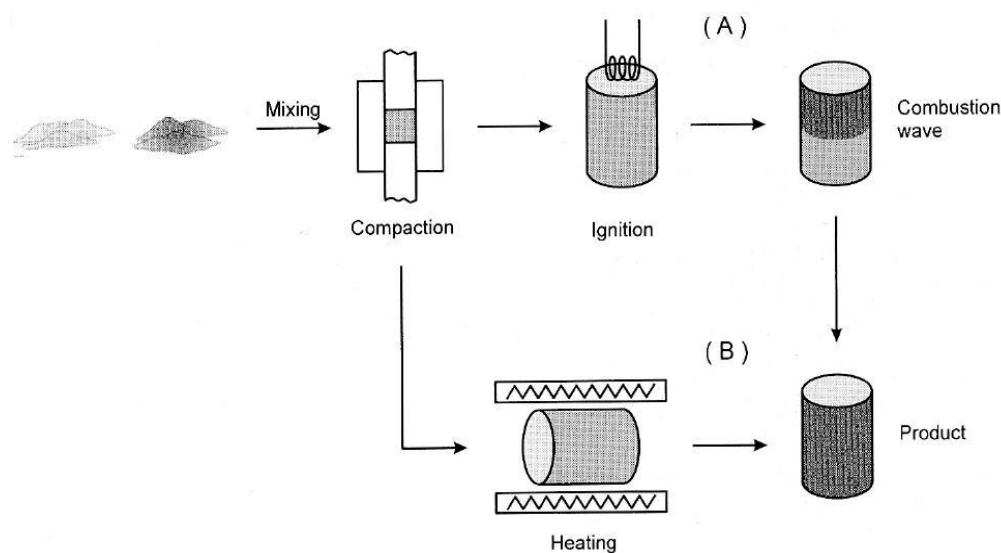
The combustion process is an exothermic redox (oxidation and reduction reactions taking place simultaneously) reaction between an oxidizer and a fuel. When the heat evolved is more than the heat required for the reaction, the system becomes self-sustained. Also the exothermicity of such reactions takes the system to a high temperature. Hence, this process, popularly known as self-propagating high temperature synthesis (SHS), is also called fire synthesis.

Combustion synthesis has emerged as an important technique for the synthesis and processing of advanced ceramics (structural and functional), catalysts, composites, alloys, intermetallics and nanomaterials. In Combustion synthesis, the exothermicity of the redox (reduction–oxidation or electron transfer) chemical reaction is used to produce useful materials. Depending upon the nature of reactants, elements or compounds (solid, liquid or gas); and the exothermicity (adiabatic temperature, T), Combustion synthesis is described as: self-propagating high temperature synthesis (SHS); low-temperature combustion synthesis (LCS), solution combustion synthesis (SCS), gel-combustion, sol–gel combustion, emulsion combustion, volume combustion (thermal explosion), etc. Combustion synthesis processes are characterized by high-temperatures, fast heating rates and short reaction times. These features make CS an attractive method for the manufacture of technologically useful materials at lower costs compared to conventional ceramic processes. Some other advantages of Combustion synthesis are:

- Use of relatively simple equipment
- Formation of high-purity products
- Stabilization of metastable phases and
- Formation of virtually any size and shape products

There are two modes where combustion synthesis can take place

- i. **Self propagating mode (A):** Self propagating high-temperature synthesis (SHS) combustion is initiated in a point, and propagates rapidly through the reaction mixture (i.e. it is due to combustion wave).
- ii. **Simultaneous combustion mode (B):** When the entire mixture is heated to the ignition temperature, reaction takes place simultaneously throughout the reactant mixture (i.e. it is due to thermal explosion).



Source: Journal of materials chemistry

Figure 2. Schematic illustration of the self-propagating combustion mode (route A) and the thermal explosion mode (route B).

As a conclusion, all the other methods mentioned above are either they need expensive equipments or the nano particles formed are not uniform compared to combustion synthesis. Gel combustion gives a high purity and high quality nano powders due to the possibility of stoichiometric control. The Process is also fast (instantaneous) and yields homogenous crystalline products with desired composition and structure.

2.2.5.1 Preparation of Metal oxides by the combustion of redox mixtures

Redox mixtures like $\text{KNO}_3 + \text{C} + \text{S}$ (gun powder) once ignited undergo self-propagating, gas-producing exothermic decomposition. Similar exothermic reactions of redox mixtures are used in rocket propellants e.g. $\text{NH}_4\text{C}_{10}\text{H}_{19}\text{N}_2\text{O}_8$ -Al-CTPB. These redox mixtures containing metallic ingredients (Mg, Al) are known to give metal oxides as undesired products of combustion. This phenomenon has now been exploited to actually synthesize metal oxides by the combustion of stoichiometric mixtures of metal nitrates (oxidizer) and urea /hydrazine-based fuels.

The stoichiometric composition of the metal nitrate (oxidizer) and fuel redox mixtures was calculated based on the total oxidizing and reducing valency of the oxidizer and the fuel which serve as a numerical coefficient for stoichiometric balance so that the equivalence ratio, Φ_e , is unity, i.e. $\text{O/F} = 1$ and the energy released is maximum.

In propellant chemistry, the species M^{2+} , M^{3+} , M^{4+} , C and H are considered to be reducing with corresponding valencies + 2, + 3, + 4, + 4 and + 1. Elemental oxygen is considered to be an oxidizing species with valency - 2. The valency of nitrogen is considered to be zero. According to this oxidizing and reducing valencies of the fuels such as urea ($\text{CH}_4\text{N}_2\text{O}$, U), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, CA), carbonylhydrazide ($\text{CH}_6\text{N}_4\text{O}_2$, CH), tetra formyl tris-azine ($\text{C}_4\text{H}_{16}\text{N}_6\text{O}_2$, TFTA), oxalyl dihydrazide ($\text{C}_2\text{H}_6\text{N}_4\text{O}_2$, ODH), maleic hydrazide ($\text{C}_4\text{H}_4\text{N}_2\text{O}_2$, MH), and malonic dihydrazide ($\text{C}_3\text{H}_8\text{N}_4\text{O}_2$, MDH) are + 6, +18, + 8, + 28, + 10, + 16, and + 16 respectively.

Stoichiometric amount of metal nitrate (oxidizer) and fuel when ignited approximately 350-500°C undergo self-propagating, gas-producing combustion reaction (smoldering or flaming) (temp. 900- 1500°C) to yield voluminous metal oxide in less than 5 min. The high in situ temperature (about 1500 °C) attained during the combustion synthesis of $\alpha\text{-Al}_2\text{O}_3$ using $\text{Al}(\text{NO}_3)_3$ -urea mixture has been attributed to the gas phase reaction of combustible decomposition products of urea

(CO, HNCO, NH₃) and the aluminum nitrate. A number of advanced ceramic oxide materials have been prepared by the combustion of metal nitrate urea/ hydrazine fuels. These include: refractory oxides such as α -alumina.

2.3 Characterization methods

The aim of characterizing nano particles is to investigate the micro-structure of nanoparticles produced by the gel combustion technique from aluminium nitrate as an oxidizer and urea/citric acid as a fuel. Nanoparticle characterization is necessary to establish understanding and control the nanoparticle synthesis and applications.

Characterization is done by using a variety of different techniques, mainly drawn from materials science. Common techniques used to characterize the nano particles are Electron Microscopy (TEM, SEM), Atomic Force Microscopy (AFM), Dynamic Light Scattering (DLS), X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffractometer (XRD), Brunnauer-Emmet-Teller (BET) and Thermo Gravimetric Analysis (TGA). The following properties of nano alumina powders will be studied in this project.

- particle size
- morphology
- crystal structure and
- surface area

The descriptions of the experimental methods used for the characterization of the nanoparticles are discussed below.

2.3.1 Scanning Electron Microscopy (SEM)

Electron microscopes were developed in the 1930s to overcome the limitations of optical microscopy and provide increased magnification and resolution, far superior to optical systems.

SEM is a powerful tool for examining and interpreting microstructures of materials, and is widely used in the field of material science. The principle of SEM is based on the interaction of an incident electron beam and the solid specimen. Electron bombardment can produce a wide variety of emissions from the specimen, including backscattered electrons, secondary electrons, Auger electrons, X-rays, visible photons and so on.

i) **Secondary Electrons:** If an incident electron collides with an electron in a sample atom, it will knock the electron out of its orbital shell and the atom will become ionized. Because the incident electron loses little energy during each collision, multiple collisions are possible, continuing until the incident electron no longer has the energy to dislodge secondary electrons. Each freed secondary electron has a very small kinetic energy (<50 eV), which is independent of the incident electron energy. If generated close enough to the sample surface (<10 nm), these secondary electrons can escape to be collected by the detector. As a direct result, secondary electron imaging is closely related to sample topography.

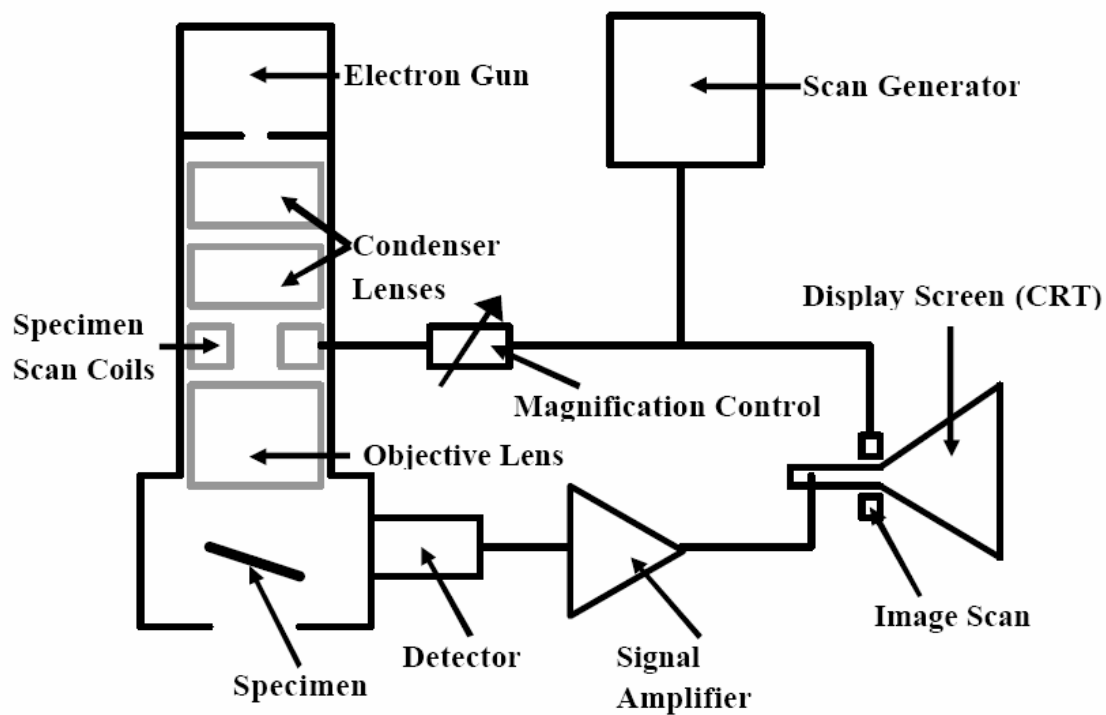
ii) **Backscattered Electrons:** If an incident electron collides with the nucleus of surface atom, the electron will bounce or scatter 'backward' out of the sample as a backscattered electron (BSE). These electrons have high energies, typically between 50 eV and that of the original incident electron. The production of backscattered electrons varies directly with atomic number, and thus backscattered electron images can be used to discern differences in sample atomic number.

iii) **Auger Electrons:** As a result of secondary electron generation, a vacancy is left in an ionized atom's electron shell. To fill this vacancy, an electron from a

higher energy outer shell (from the same atom) can drop down to fill the vacancy. This creates an energy surplus in the atom that can be corrected by emitting an outer electron, an Auger electron. Auger electrons have a characteristic energy unique to the element from which they are emitted and can be used to give compositional information about the target sample. Auger electrons have a relatively low kinetic energy and are only emitted from shallow sample depths(<3 nm).

iv) **Characteristic X-rays:** X-rays are also produced by interactions of the incident electron beam with a sample surface. Similar to the Auger electron generating process, the excess energy produced by reshuffling electrons to fill shell vacancies can also be emitted in the form of an X-ray rather than an Auger electron. X-rays have a characteristic energy unique to the element from which they originate and so provide compositional information about a sample. Secondary electron imaging and X-ray analysis were the primary functions used for SEM sample characterization in this study.

An SEM consists of three distinct parts: an electron column; a detection system; and a viewing system. Figure 3 below shows a schematic of a simple scanning electron microscope. Two electron beams are controlled simultaneously by the same scan generator: one is the incident electron beam; the other is for the cathode ray tube (CRT) screen. The incident beam is scanned across the sample, line by line, and the signal from the resulting secondary electrons is collected, detected, amplified and used to control the intensity of the second electron beam. Thus a map of intensity of secondary electron emission from the scanned area of the sample will be shown on the CRT screen as variations in brightness, reflecting the surface morphologies of the specimen. Given this mechanism, the magnification of the SEM image can be adjusted simply by changing the dimensions of the area scanned on the sample surface.



Source: <http://www.chm.bris.ac.uk/pt/diamond/lithesis/Chapter%203.pdf>

Figure 3. Schematic diagram of a scanning electron microscope

2.3.2 X-ray Powder Diffraction (XRD)

X-ray diffraction (XRD) is one of the techniques used for the characterization of crystalline solids and determination of their structure. About 95% of all solid materials can be described as crystalline and when X-rays interact with a crystalline phase, a diffraction pattern is generated as a result of the interaction between the incident X-rays and the atomic architecture of the solid. Each crystalline solid has unique atomic architecture and consequently has a unique characteristic X-ray powder pattern. These patterns can be used as ‘fingerprints’ for identification of solid phases. Once the material has been identified-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and the size and the shape of the unit cell, etc.

When X-rays interact with atoms in two lattice planes, and the path length difference between rays equals a whole multiple of the wavelength of the radiation, constructive interference occurs (Figure 4). Bragg's law describes the conditions for constructive interference in certain directions and the production of diffracted scattered X-rays:

$$n\lambda = 2d \sin\theta$$

Where,

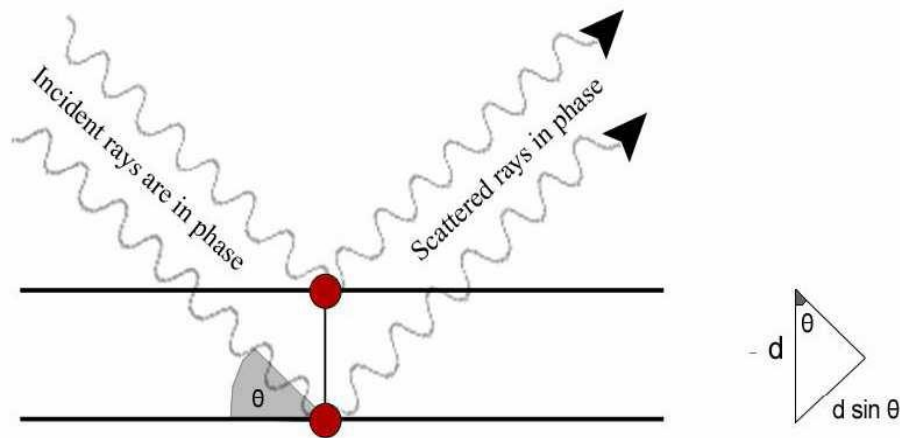
n = an integer,

λ = the wavelength of the X-rays

d = the spacing between 2 atom layers

θ = the angle between the incoming X-ray and the atom layer.

The relation by which diffraction occurs is known as Bragg's law.



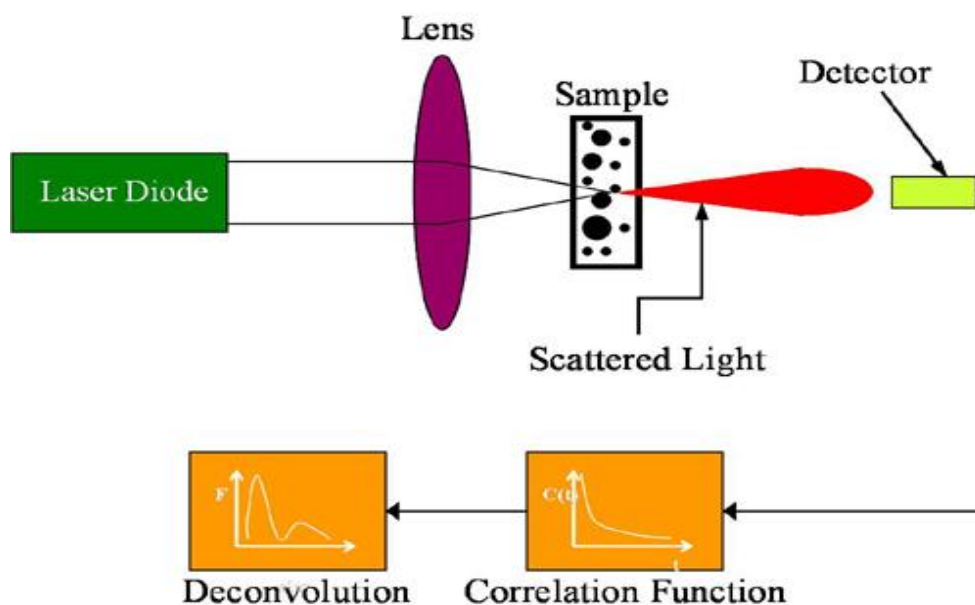
Source: <http://www.chm.bris.ac.uk/pt/diamond/lithesis/Chapter%203.pdf>

Figure 4. An X-ray diffraction beam schematic , showing the incident and scattered X-rays, from a pair of atoms in different lattice planes.

This is the basic relationship among the spacing between the lattice planes (d-spacing), the wavelength and the angle (θ) of observation in a diffraction experiment. The angle between the incident and diffracted beams is 2θ degrees.

2.3.3 Dynamic light scattering (DLS)

Dynamic Light Scattering is also known as Photon Correlation Spectroscopy. This technique is one of the most popular methods used to determine the size of particles. It measures the intensity of light scattered by particles in the sample. Figure 5 below shows a systematic diagram of a dynamic light scattering.



Source: <http://www.chem.agilent.com/en-US/Products/Instruments/particleanalysis/pages/dlsbasics.aspx>

Figure 5: systematic diagram of a dynamic light scattering

When a beam of light passes through a colloidal dispersion, the particles or droplets scatter some of the light in all directions. When the particles are very small compared with the wavelength of the light, the intensity of the scattered light is uniform in all directions (Rayleigh scattering); for larger particles (above approximately 250nm diameter), the intensity is angle dependent (Mie scattering)

If the light is coherent and monochromatic, as from a laser for example, it is possible to observe time-dependent fluctuations in the scattered intensity using a suitable detector such as a photomultiplier capable of operating in photon counting mode.

These fluctuations arise from the fact that the particles are small enough to undergo random thermal (Brownian) motion and the distance between them is therefore constantly varying. Constructive and destructive interference of light scattered by neighboring particles within the illuminated zone gives rise to the intensity fluctuation at the detector plane which, as it arises from particle motion, contains information about this motion. Analysis of the time dependence of the intensity fluctuation can therefore yield the diffusion coefficient of the particles from which, via the Stokes Einstein equation, knowing the viscosity of the medium, the hydrodynamic radius or diameter of the particles can be calculated.

The size of a particle is calculated from the translational diffusion coefficient by using the Stokes-Einstein equation;

$$d(H) = \frac{kT}{3\pi\eta D}$$

where,

$d(H)$ = hydrodynamic diameter

D = translational diffusion coefficient

k = Boltzmann's constant

T = absolute temperature

η = viscosity

The time dependence of the intensity fluctuation is most commonly analysed using a digital correlator. Such a device determines the intensity autocorrelation function which can be described as the ensemble average of the product of the signal with a delayed version of itself as a function of the delay time. The "signal" in this case is the number of photons counted in one sampling interval. At short delay times, correlation is high and, over time as particles diffuse, correlation diminishes to

zero and the exponential decay of the correlation function is characteristic of the diffusion coefficient of the particles. Data are typically collected over a delay range of 100ns to several seconds depending upon the particle size and viscosity of the medium.

Analysis of the autocorrelation function in terms of particle size distribution is done by numerically fitting the data with calculations based on assumed distributions. A truly mono disperse sample would give rise to a single exponential decay to which fitting a calculated particle size distribution is relatively straightforward.

Particle size distributions can be calculated either assuming some standard form such as log-normal or without any such assumption. In the latter case, it becomes possible, within certain limitations, to characterize multimodal or skewed distributions. The size range for which dynamic light scattering is appropriate is typically submicron with some capability to deal with particles up to a few microns in diameter. The lower limit of particle size depends on the scattering properties of the particles concerned (relative refractive index of particle and medium), incident light intensity (laser power and wavelength) and detector / optics configuration.

Dynamic light scattering is particularly suited to determining small changes in mean diameter such as those due to adsorbed layers on the particle surface or slight variations in manufacturing processes. DLS is an absolute measurement where knowledge of the particle composition is not needed. It can generally measure particles ranging in size from 1 nm to 1000nm.

CHAPTER 3

METHODOLOGY

3.1 Chemicals /equipments required

The chemical and equipments required for this research are shown in Table 1 and Table 2 respectively.

Table 1.Raw material characteristics

Raw materials	Formulation	Molecular Weight (g/mol)	Purification (%)	Physical state	Manufacturer
Aluminum nitrate	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	375.117	99	Solid	MERCK
Urea	NH_2CONH_2	60.00	99	Solid	MERCK
Citric acid	$\text{C}_6\text{H}_8\text{O}_7$	192.13	99	Solid	MERCK
Ammonia	NH_3	17.031	60	Liquid	MERCK

Table 2. Equipments required for the experiment and characterization.

Equipments	Purpose
SEM	Morphology
XRD	Crystal structure
DLS	Particle size determination
Glass apparatus	Sample preparation
PH meter	PH control
Crucible	To put the gel in the furnace
Hot plate	Heating the solution

3.2 Experimental procedure

The following diagram (Figure 6) shows the experimental procedure nano alumina synthesis by gel-combustion method.

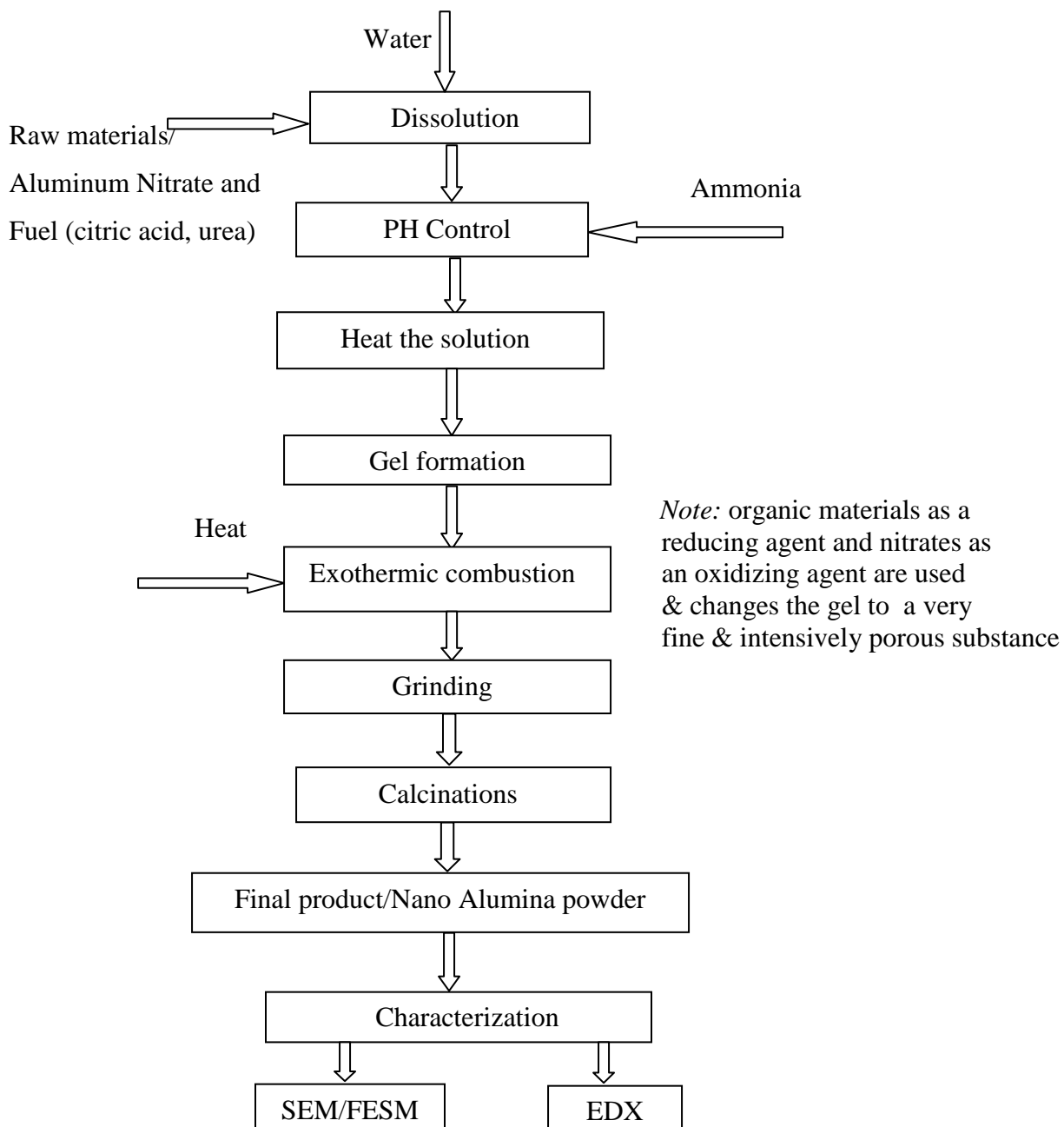


Figure 6: Experimental steps for the synthesis of nano alumina and its characterization.

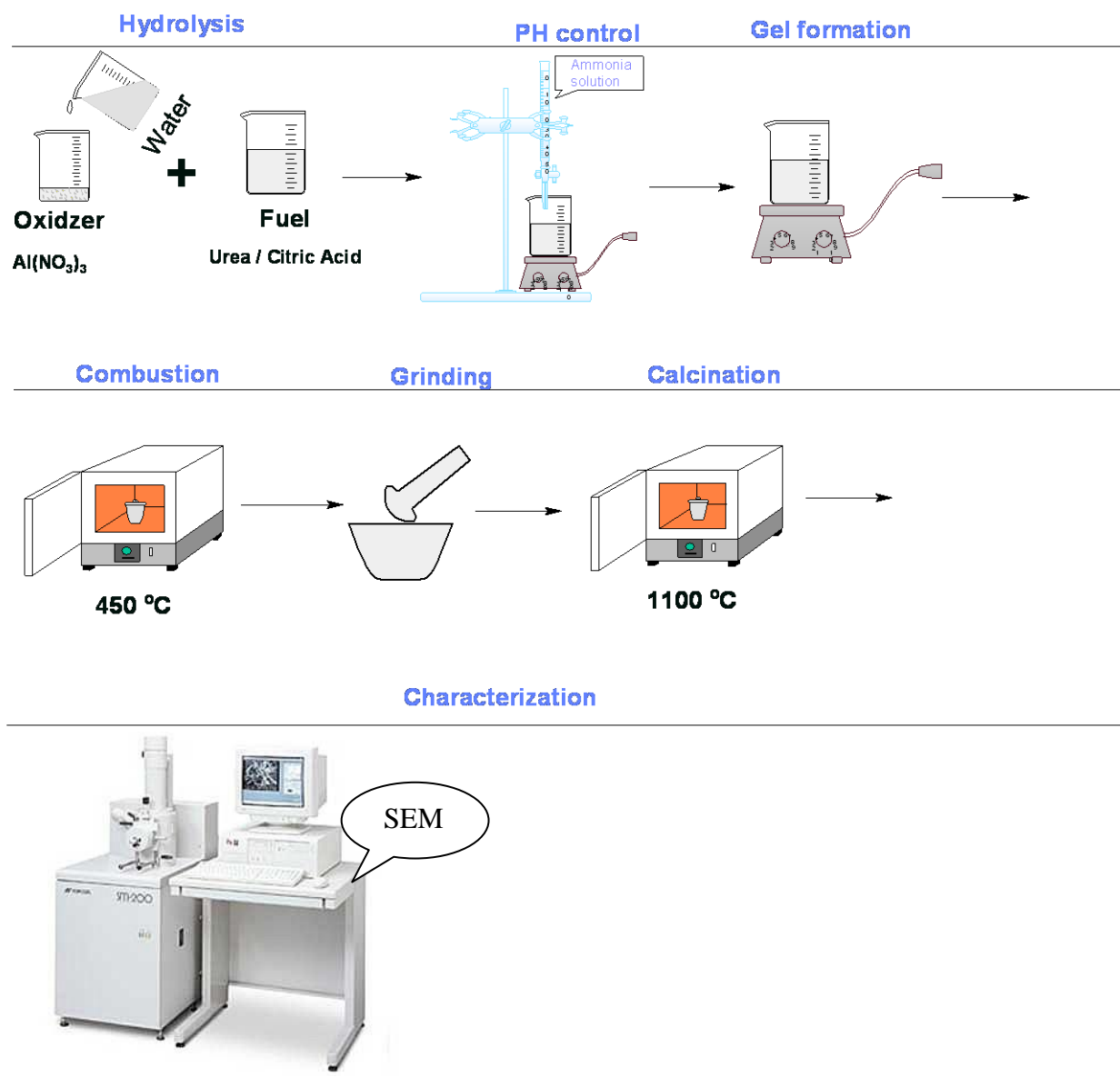


Figure 7. Graphical flowchart for the combustion synthesis and characterization of nano sized alumina (Al_2O_3).

3.3 Sample preparation

For the design of the experiments, a two level screening design was utilized for investigating and sorting the effective factors on combustion synthesis of alumina powders. The first step is selection of factors. The type of fuel, fuel to oxidizer ratio and pH of the starting solution are the factors selected for study in this research.

The second step is determination of high and low levels for each factor. The initial composition of the solution containing aluminum nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and urea was derived from the total oxidizing and reducing valences of the oxidizer and fuel using the concepts of propellant chemistry. Carbon, hydrogen and aluminum were considered as reducing elements with the corresponding valences of +4, +1 and +3, respectively. Oxygen was considered as an oxidizing element with the valence of 2, the valence of nitrogen was considered to be 0. The total calculated valence of metal nitrates by arithmetic summation of oxidizing and reducing valences was -15 . The calculated valence of urea was $+6$. The stoichiometric composition of the redox mixture demanded that $1(-15) + n(+6) = 0$, or $n = 2.5$ mol. This calculation was also done for mixture of aluminum nitrate and citric acid, so the stoichiometric composition of the redox mixture demands that $1(-15) + n(+18) = 0$, or $n = 0.83$ mol (refer Appendix A). Selected levels for fuel to oxidizer ratio were stoichiometric amount (St) and $1.4 \times St$. In this study, the type of main fuels was a qualitative factor and urea and citric acid were high and low levels respectively; Other factors investigated were pH of the starting solution. A PH value of 3 and 10 were chosen as low and high level respectively, which is adjusted by adding ammonia solution.

Table 3. Factors and levels

Factor	Allocated letter	High level	Low level
Fuel to oxidizer ratio	A	1.5*St	St
Type of fuel	B	urea	Citric acid
PH of the starting solution	C	10	3

Table 4. Combination of factors and levels of the samples

sample	sample code	A	B	C
1	U1	1	Urea	3
2	U2	1	Urea	10
3	C1	1	Citric acid	3
4	C2	1	Citric acid	10
5	U3	1.5	Urea	3
6	U4	1.5	Urea	10
7	C3	1.5	Citric acid	3
8	C4	1.5	Citric acid	10

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Initial observations

Combustion synthesis using aluminium nitrate ($\text{Al}(\text{NO}_3)_3$) was performed using both urea and citric acid as fuels in the redox mixture. The citrate–nitrate gel synthesis follows a series of oxidation and redox reactions to finally yield an ash. When the precursor solution (mixed solution of the metal nitrate and citric acid) is heated at around 100–200 °C, dehydration takes place followed by gelation. The gelation probably results due to the formation of a metal–citrate–nitrate complex. On continued heating, the decomposition of the nitrates takes place with the evolution of gases like NO_2 , NO , and N_2O_5 . The resulting swelling and effervescence of the gel is accompanied by the evolution of brown gases (NO_x type) during this stage. This reaction is followed by the formation of a metal–citrate complex in the form of a black ash, which is the end product of the synthesis. The same phenomena occurred when urea is used as a fuel except that the powder obtained after the combustion is white.

4.2 EDX

The Energy Dispersive X-ray (EDX) analysis is conducted to identify the elemental composition of each sample. Figure 8 and 9 below shows that, the carbon content when citric acid used as a fuel is higher than that of urea in general.

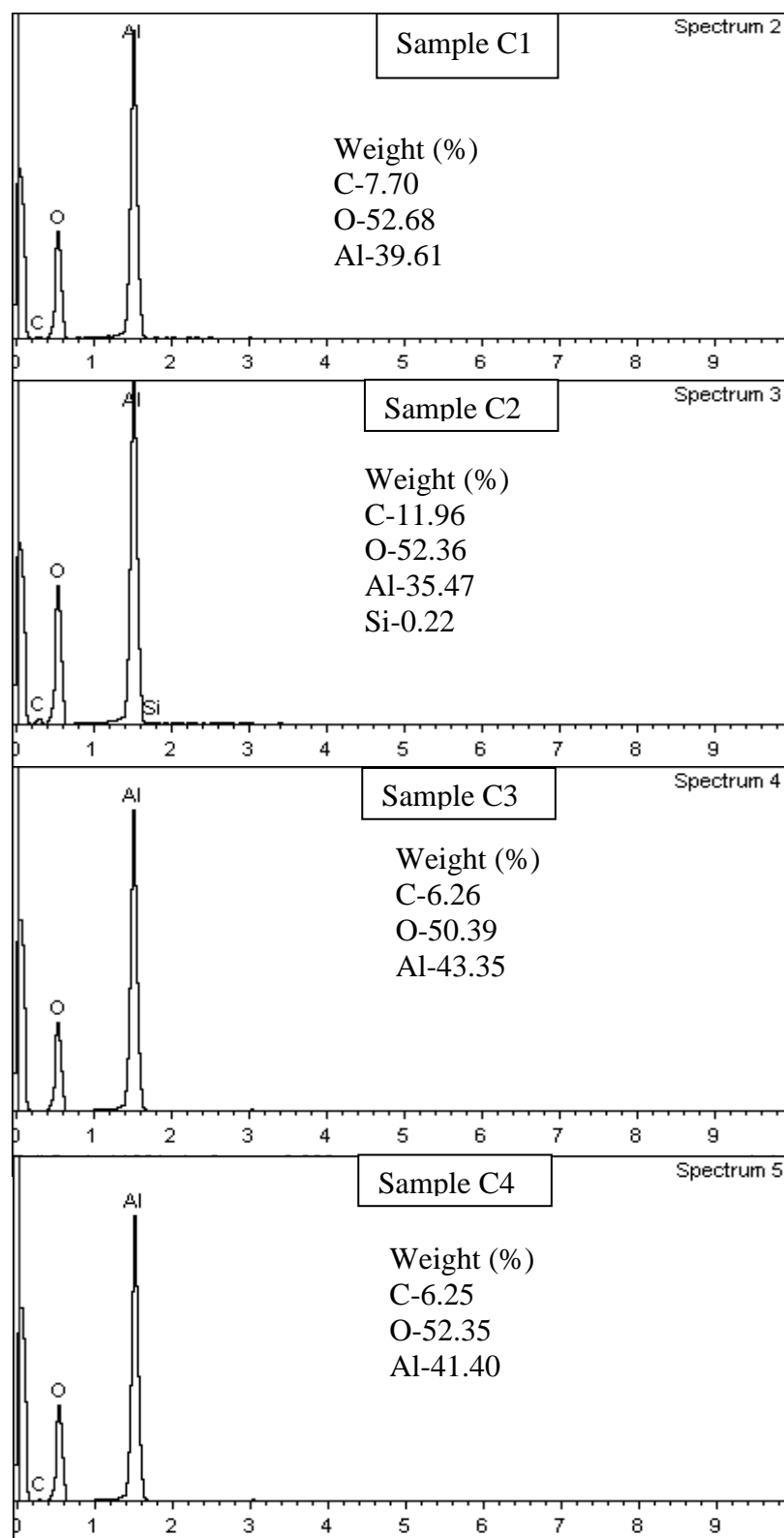


Figure 8. EDX analysis of the samples prepared using citric acid as a fuel

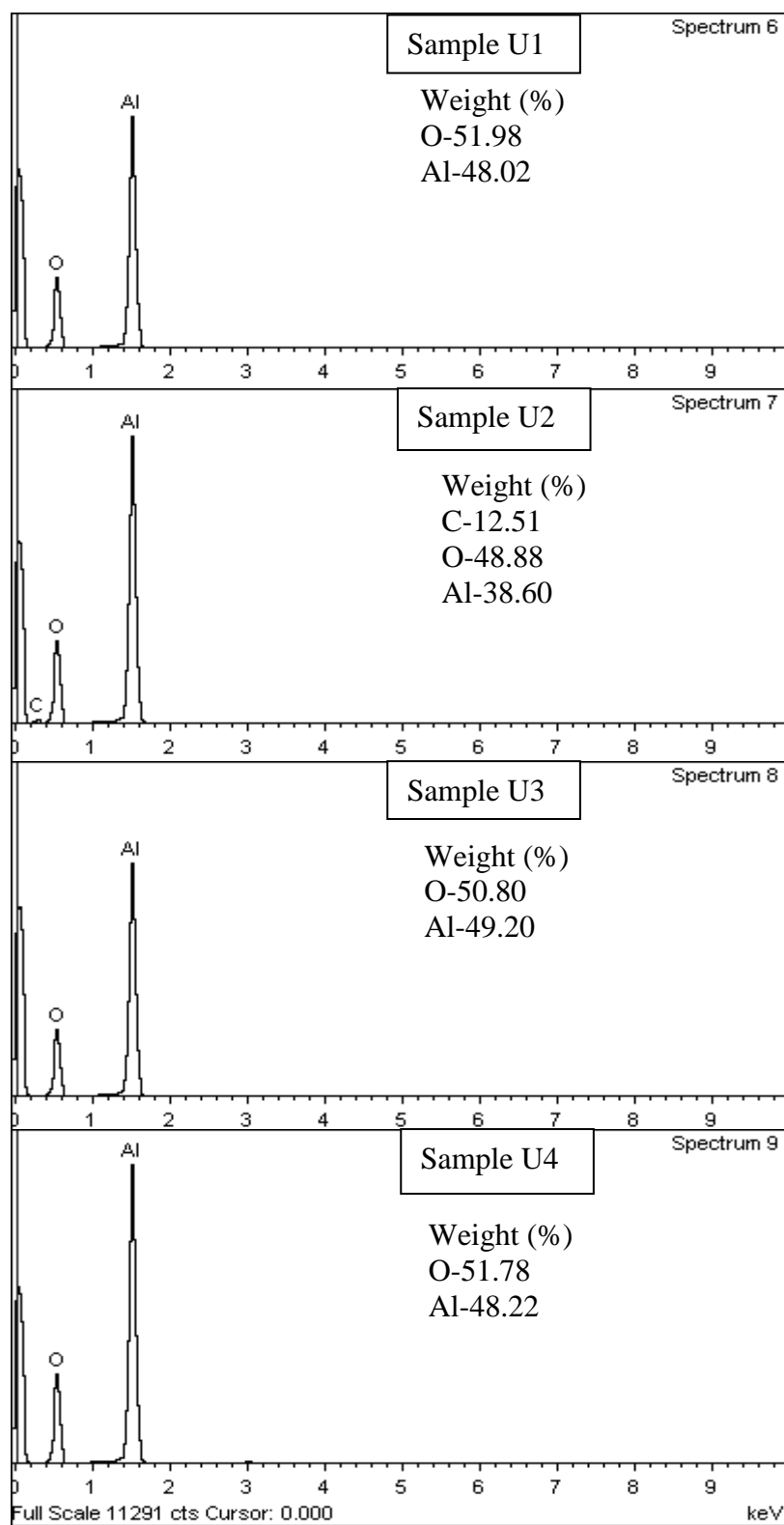


Figure 9. EDX analysis of the samples prepared using urea as a fuel

Except sample U2, all the samples prepared using urea as a fuel gives pure alumina. Therefore, it can be concluded that preparing alumina using urea is best in terms of purity of alumina from carbon.

4.3 Particle size

The particle size of the nano alumina is determined using scanning electron microscope (SEM). The particle size of all the samples with their specific parameters is presented in table 5.

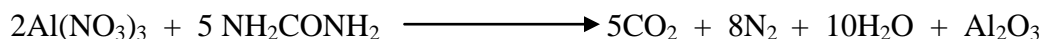
Table 5.The particle size of all the samples measured using SEM

Sample code	Aluminum nitrate	Fuel-urea/acetic acid	Average Particle size (nm)
U1	15	6	117
U2	15	6	89
C1	15	6.4	130
C2	15	6.4	182
U3	15	9	197
U4	15	9	156
C3	15	9.6	175
C4	15	9.6	169

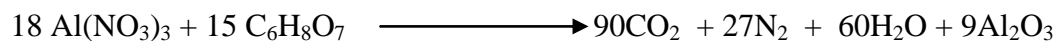
The effect the three factors on the particle size of nano alumina is discussed below.

4.3.1 Effect of the type of fuel

There are two types of fuel used in this experimental work which are urea and citric acid. These two fuels have different properties even though they both are organic chemicals. Citric acid is rich in its carbon content whereas urea has less percentage of carbon. The combustion reaction involving aluminum nitrate and urea may be represented as follows:



Where as, the combustion reaction involving aluminum nitrate and citric acid may be represented as follows:



As we can see from Table 5, the particle size obtained using urea as a fuel shows smaller size in general as compared with citric acid. This is due to the reason that the heat released during combustion is relatively low for citric acid, the combustion reaction is incomplete. The carbon content of the products synthesized using citric acid as a fuel is higher than that using urea. That is the reason why the ash produced using citric acid at 450°C is black and converted to white during calcinations at 1100°C.

4.3.2 Effect of fuel to oxidizer ratio

In order to understand the role of oxidant-to-fuel ratio, the powder properties obtained using urea and citric acid as fuels, were compared (Table 5). It was observed that in case of combustion using urea as the fuel, in fuel ratio at stoichiometric, finest crystallites for alumina were obtained, whereas the fuel excess ratio (1.5st) yielded the largest crystallite sizes. This observation can be explained based on the flame temperatures associated with combustion reactions. The flame temperature associated with stoichiometric combustion is higher, whereas the fuel-excess combustion reaction gave rise to a lower temperature. Thus, higher the flame temperature, higher the crystallite size and smaller is the surface area.

However, in the case of citric acid as fuel, it was observed that the stoichiometric ratio (st) resulted in the finest crystallites of this alumina oxide as compared to that obtained by the fuel excess ratio (1.5st). This observation can be attributed to the fact that in case of citric acid taken in the stoichiometric ratio, there is more

number of gaseous products, which fragment the product while escaping, to give finer particles. It appears that the superior powder properties in case of stoichiometric ratio of citric acid are due to the dominant effect of number of gas molecules over the flame temperature.

4.3.3 Effect of PH

Adjustment of pH was done by addition of ammonia solution. Addition of this material would change the concentration of nitrate ions, and it can change the amount

4.4 SEM

A LEO 1430VP electron microscopy was used to take the SEM view of the samples at magnification of 15000x. The SEM photographs of all the samples are given in the sections below.

4.4.1 Effect of the type of fuel

The microstructures of samples with different fuels are shown in Fig. 10. From the SEM microstructures, it is possible to find out that urea to aluminum nitrate at stoichiometric ratio and PH value 10 gave better result. Therefore, it is possible to suggest that using urea can bring down the formation temperature of the product due to the easier complex formation and homogeneous gel, thus the crystallite sizes are smaller in comparison to citric acid. When citric acid was used, the ash formed in the muffle furnace at 500°C is black. It occurred because of the content of carbon and it is converted to white during calcinations at 1100°C. Therefore, the heat released during combustion is more and as a result the combustion reaction enthalpy is more which yields a growth of the crystallite size with a complete combustion reaction.

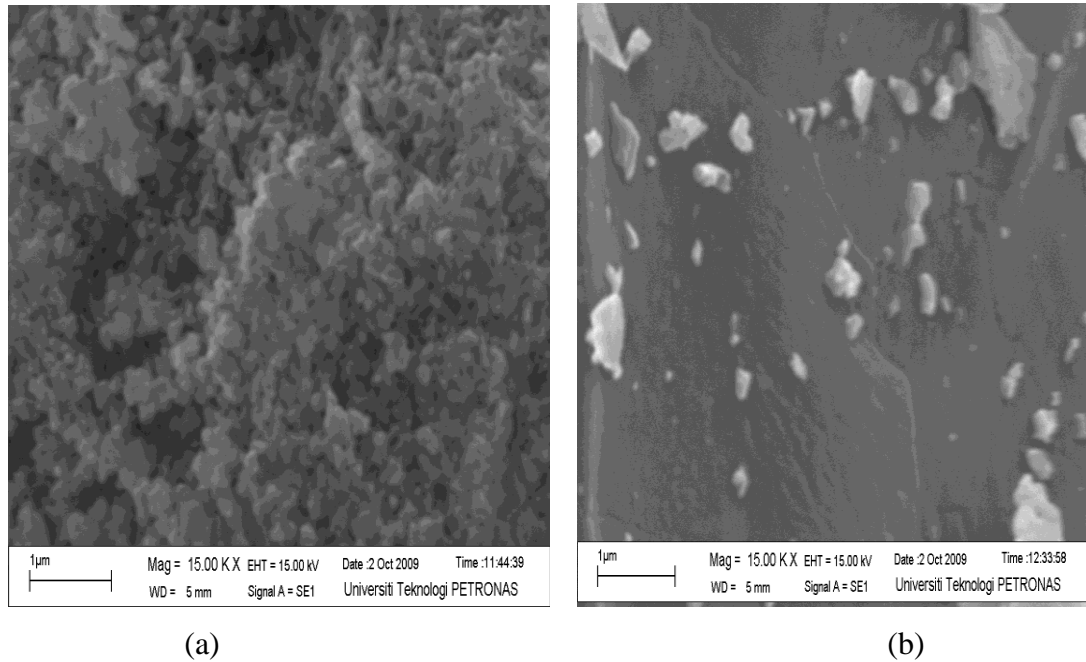
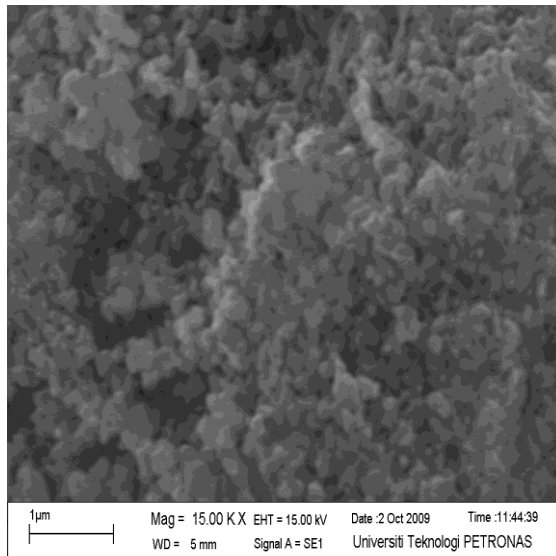


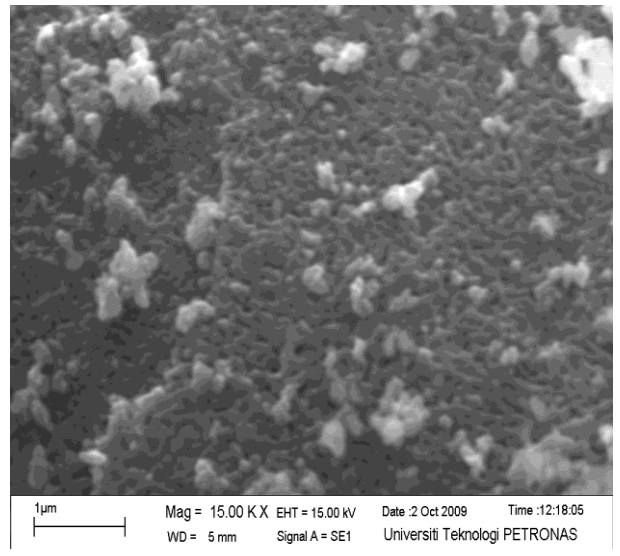
Figure 10. SEM pictures of Al_2O_3 nano powders using different fuels (a) Urea, (b) Citric acid.

4.4.2 Effect of fuel to oxidizer ratio

Figure 11 shows the SEM micrographs of the 1100 °C calcined alumina powder from gels with different urea to nitrate ratios of stoichiometric ratio (st) and fuel excess ratio (1.5st). It can be seen that the morphology of sample U2 (refer fig 11a.) which is synthesized at stoichiometric ratio, is uniform and fine but the morphology of sample U2 (refer fig 11b.) which is synthesized in urea excess ratio, shows the development of large crystal. It can be concluded that the increment of the fuel to oxidizer ratio at large has a negative impact on the synthesis of nano alumina.



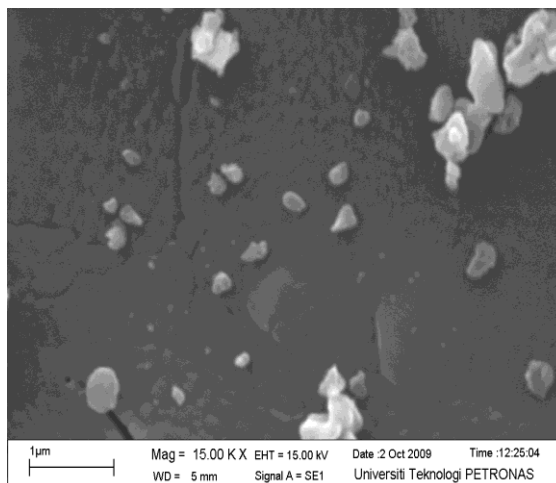
(a)



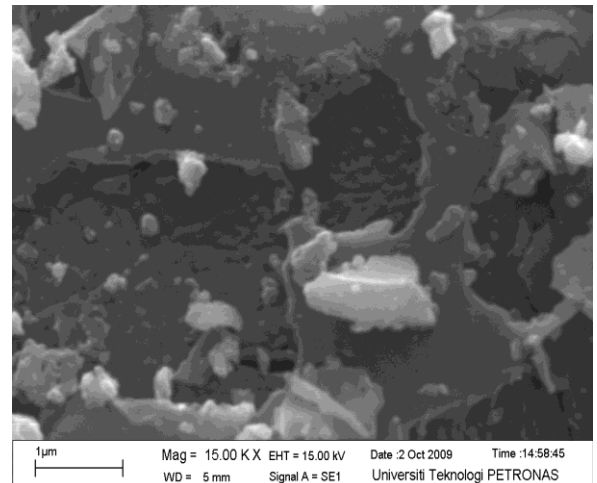
(b)

Figure 11. SEM pictures of Al_2O_3 nano powders in two different fuel (urea) to oxidizer ratio of (a) st, (b) 1.5st

In the case of citric acid as fuel (refer fig 12), it was observed that the stoichiometric ratio (st) resulted in the fine crystallites of this alumina oxide as compared to that of the particles obtained by the fuel excess ratio (1.5st).



(a)



(b)

Figure 12. SEM pictures of Al_2O_3 nano powders using different fuel (citric acid) to oxidizer ratio of (a) st, (b) (1.5st)

4.4.3 Effect of PH

Adjustment of the PH was done by the addition of ammonia. Addition of this material would change the concentration of the nitrate ions, and it can change the amount of fuel to oxidizer ratio. The increase of nitrate ions in the low PHs is expected to decrease the enthalpy of the exothermic reaction by decreasing the fuel to oxidizer ratio. Thus the rate of combustion reaction would decrease and in this condition alumina particles come close to foam and agglomeration will increase (Pathak, 2002).

The first two samples (U1 and U2) prepared using urea as a fuel at stoichiometric (st) ratio and PH value of 3 and 10. It can be seen that the sample U2 (refer fig 13b) has a uniform particle size due to the existence of enough ammonia for the combustion process. On the other hand, sample U1 (refer fig 13a) shows a lack of uniformity since the process is took place at a lower PH.

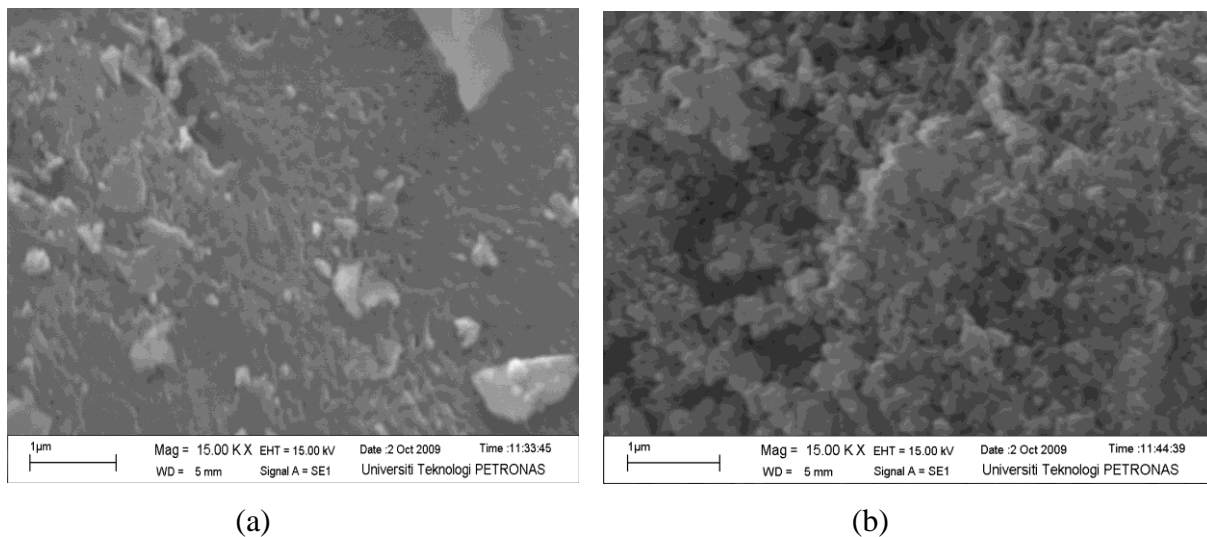


Figure 13. SEM pictures of Al_2O_3 nano powders prepared using urea and different PH value of (a) PH=3, (b) PH=10

The impact of PH on the morphology when citric acid is used as fuel is not that vital. As it can be observed from figure 14, the micrograph of both samples is more or less similar unlike the samples U1 and U2 where they show high difference.

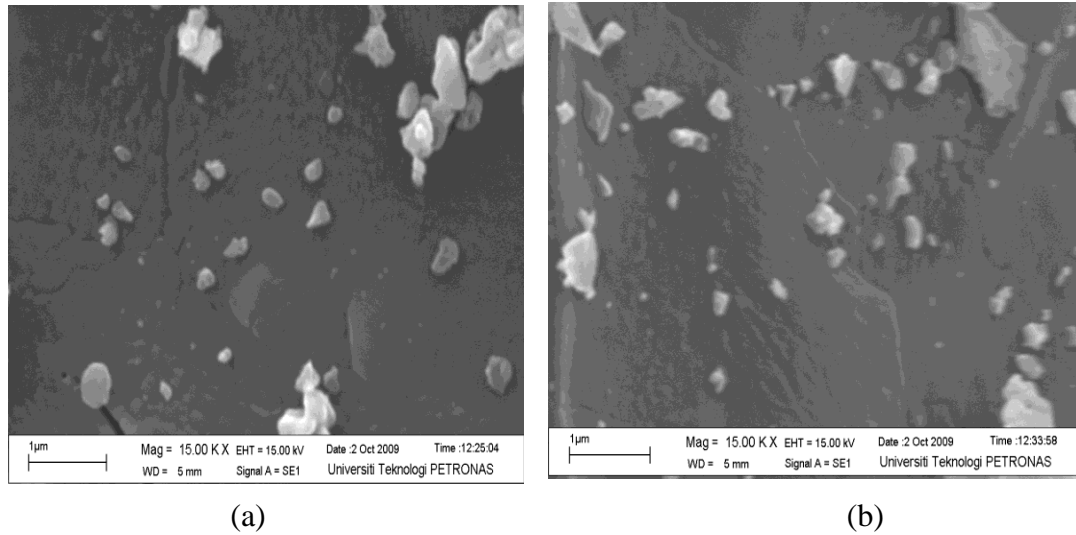


Figure 14. SEM pictures of Al_2O_3 nano powders prepared using citric acid and different PH value of (a) PH=3, (b) PH=10

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This paper reports the synthesis of nano-crystalline alumina powder by the gel combustion process of a urea/citric acid-aluminum nitrate precursor gel and the effect of variation of type of fuel, fuel to oxidizer ratio and PH of starting solution on the decomposition characteristics of the corresponding gel samples. The result shows that urea is a better fuel as compared with citric acid for the synthesis of alumina. Stoichiometric and off-stoichiometric fuel to oxidizer ratios were selected for this purpose. It was found that the decomposition nature of the gel and the characteristics of the resultant powder could be controlled by careful control of the fuel-oxidizer ratio in the gel. The best results when urea was used as a fuel was obtained at a stoichiometric ratio and PH value of 10 where as, for citric acid-a better result was found at 1.5 of ratio of fuel to oxidizer and PH value of 10. Generally, a dependence of all the three parameters on both the morphology and the particle size of the alumina powders *calcined* at 1373 K have been noticed. This gel combustion of the urea/citrate-nitrate gel is a very simple and convenient route to produce alumina by proper choice of the type of fuel, fuel to oxidizer ratio and PH of the starting solution. Thus, the preparation of nano-crystalline oxide ceramics by a simple and cost-effective solution combustion process, for the powder property-functionality correlation, is a wide area of interest and further research.

5.2 Recommendation

This Experimental study on the synthesis and characterization of nano alumina by gel combustion method is limited to the three parameters (type of fuel, PH and oxidizer to fuel ratio). It is recommended that other parameters should also be considered such as calcinations rate and also the performance of this gel combustion process can be increased by adding another type of fuel. In that case, the type of added fuel and molar ratio of added fuel to the main fuel will be the parameters to be studied. The number of samples for each parameter in this research is limited to two. Taking many samples for each parameter enables to study the effect thoroughly. In addition to that, the investigation of reaction mechanism, combustion temperature, the characteristic analysis of products, etc. can be investigated.

The characterization technique used for particle size in this study is SEM. This equipment doesn't reflect the overall particle size of the sample. Therefore, measuring the particle size using dynamic light scattering (DLS) or zeta sizer is far much better. Based on the need of application, other feature of the samples like surface area can also be studied. For example, if alumina is required to be used as a catalyst, the surface area needs to be high.

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APPENDICES

Appendix A

Stoichiometric or equivalence ratio (Φ_e , O/F) calculation

Urea as a fuel

The molecular weight of urea-NH₂CONH₂ is 60g/mol

The molecular weight of nano hydrated Aluminum nitrate-Al(NO₃)₃.9H₂O is 375.117 g/mol

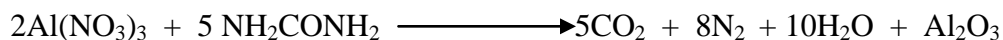
Table 6.Stoichiometric ratio calculation when urea is used as a fuel

Oxidizing valency -(Al(NO ₃) ₃)	Reducing valency- NH ₂ CONH ₂
1Al=+3	1C=+4
3N=0	4H=+4
9O=-18	2N=0
	1O=-2
Total=-15	Total=+6

$$\Phi_e \text{ (O/F)} = 15/6 = 2.5$$

i.e For every one mole of Al(NO₃)₃ ,2.5 moles of urea are required

The reaction of the combustion reaction is



Citric acid as a fuel

The molecular weight of citric acid-C₆H₈O₇ is 192.124 g/mol

The molecular weight of nano hydrated Aluminum nitrate-Al(NO₃)₃.9H₂O is 375.117 g/mol.

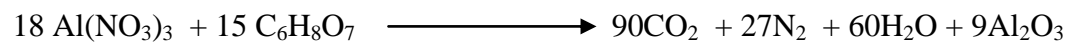
Table 7.stoichiometric ratio calculation when citric acid is used as a fuel

Oxidizing valency -(Al(NO ₃) ₃)	Reducing valency- C ₆ H ₈ O ₇
1Al=+3	6C=+24
3N=0	8H=+8
9O=-18	7O=-14
Total=-15	Total=+18

$$\Phi_e (O/F)=15/18=0.833$$

i.e For every one mole of $\text{Al}(\text{NO}_3)_3$, 0.833 moles of citric acid are required

The reaction of the combustion reaction is



Note: Calculation of the Stoichiometric ratio is used as a bench mark for the preparation of the samples.

Appendix B

Gel formation

A white gel formed from a sample prepared using 20 g of Aluminium nitrate and 8g of urea.

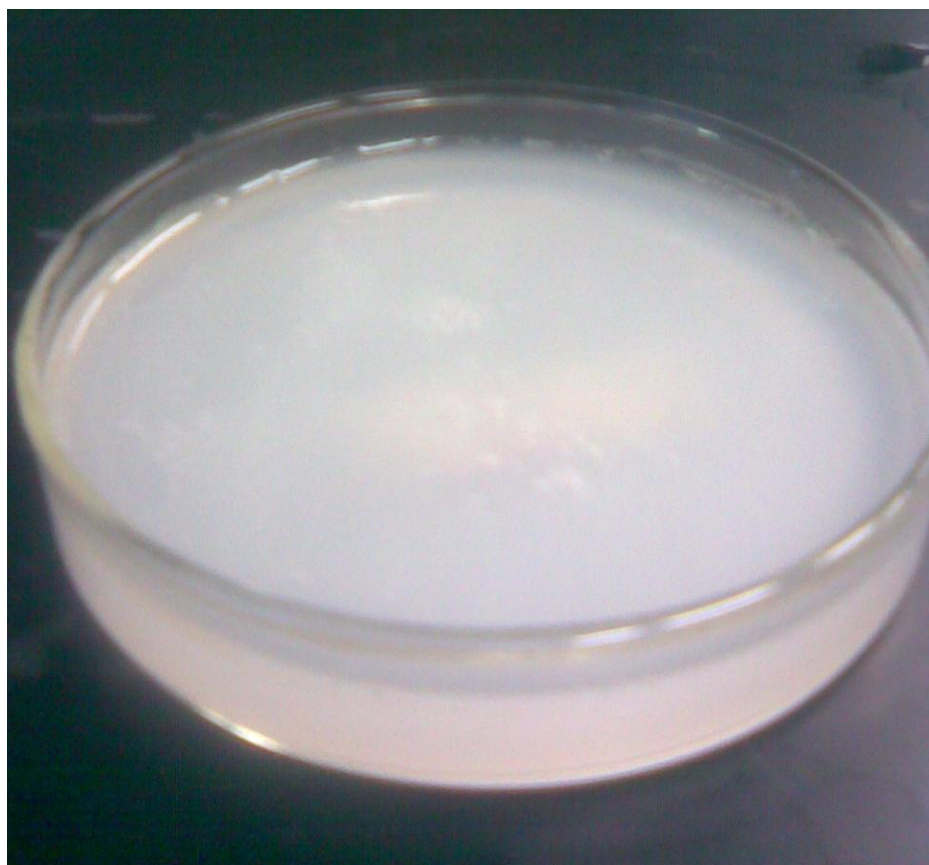


Figure 15.A white gel formed when urea and aluminium nitrate used as a starting material.

Appendix C

Synthesized alumina powder



Figure 16. The eight samples powder synthesised by gel combustion method.

The top four crucibles contain alumina synthesized using urea but at different PH and fuel to aluminium nitrate ratio and the bottom four are using citric acid as a fuel.

Appendix D

Scanning Electron Microscope (SEM)



Figure 17. Scanning electron microscope